

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : ION KOGAKU SHINKO ZAIDAN

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(72)Inventor : KOKUBO TADASHI
YAMAMOTO KOJI
MIYAJI FUMIAKI

(54) ANTIBACTERIAL GLASS AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain antibacterial colorless glass excellent in chemical durability and controlled releasability of an antibacterial material by incorporating an antibacterial metallic ion into an $\text{SiO}_2\text{-MxOy}$ glass (M is a metallic atom with the valance number less than the coordination member, and x and y are an atomic ratio of M to O).

SOLUTION: M is ≥ 1 kind of metallic atom selected from Al, La, Y, Ti, Zr, Nb and Ta. The atomic ratio (metallic M to antibacterial metal) is controlled to ≥ 1 . The glass with Al as M and Ag as antibacterial metal, for example, is produced by mixing the solns. contg. a hydrolyzable organosilicon compd., a hydrolyzable metallic M compd., the salt of an antibacterial metal and water, gelling the mixture and calcining the gel.

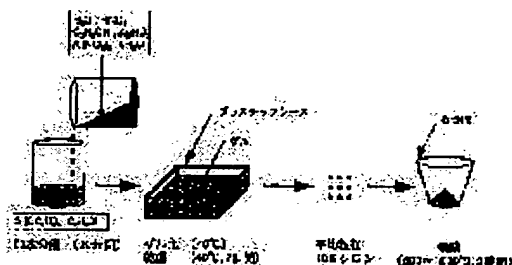
The antibacterial glass is produced as shown in the figure.

Ethanol is added to tetraethoxysilane as a solvent.

Separately, water, nitric acid, ethanol, silver nitrate and aluminum nitrate nonahydrate are mixed to form two solns.

Both solns. are mixed, the mixture is agitated for 30min and

hydrolyzed to obtain a sol, the sol is gelled, and the gel is dried, crushed and calcined.



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CLAIMS

[Claim(s)]

[Claim 1]Antimicrobial glass which is $\text{SiO}_2\text{-M}_X\text{O}_Y$ (however, as for metal atom [with few the valence than the coordination number], and X and Y, M shows atomic ratio of M and O, respectively.) system glass, and is characterized by containing an antibacterial metal ion.

[Claim 2]The antimicrobial glass according to claim 1 whose M is one or more sorts chosen from among aluminum, La, Y, Ti, Zr, Nb, and Ta.

[Claim 3]The antimicrobial glass according to claim 1 or 2 which is atomic ratio $M/(\text{antibacterial metal}) \geq 1$.

[Claim 4]The antimicrobial glass according to any one of claims 1 to 3 whose M is aluminum and whose antibacterial metal is Ag.

[Claim 5]A manufacturing method of antimicrobial glass which mixes a raw material solution containing a salt and water of an organic silicon compound of hydrolysis nature, a metal M compound (however, M shows a metal atom with few the valence than the coordination number when it becomes an oxide.) of hydrolysis nature, and an antibacterial metal, and is characterized by calcinating after gelling.

[Claim 6]A manufacturing method of the antimicrobial glass according to claim 5 whose M is one or more sorts chosen from among aluminum, La, Y, Ti, Zr, Nb, and Ta.

[Claim 7]A manufacturing method of the antimicrobial glass according to claim 5 or 6 which is atomic ratio $M/(\text{antibacterial metal}) \geq 1$.

[Claim 8]A manufacturing method of the antimicrobial glass according to any one of claims 5 to 7 whose M is aluminum and whose antibacterial metal is Ag.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention belongs to antimicrobial glass and a manufacturing method for the same. The antimicrobial glass of this invention is used suitably for the germicide of the filler of composite resin for dentistry restoration, the filler of cement for body bone restoration, the filler of a catheter, a paint, and water, etc., and it deals in it.

[0002]

[Description of the Prior Art]Conventionally, as a manufacturing method of antimicrobial glass, scorification, ion implantation, and a sol gel process are known as state-of-the-art art before this application. Scorification mixes with silver oxide powder, such as silicic acid which is a general glass manufacturing method, for example, serves as raw materials for glass, and way acid, and after it fuses, it quenches and vitrifies it.

[0003]Ion implantation accommodates beforehand the glass which is the target of an ion implantation in the chamber of ion implantation equipment, and is a method of pouring the ion of antibacterial substances, such as silver, into the glass.

An ion implantation is carried out by heating and steam-izing an antibacterial substance, supplying a silver steam to inter-electrode [in a vacuum], and ionizing it (JP,6-211619,A).

[0004]A sol gel process is the method of hydrolyzing the reactant of metal alkoxide compounds, such as tetraethyl silicate, and the silver coordinated complex which configures alkoxy group content compounds, such as trimethoxysilylpropyl diethylenetriamine, adjusting a gel object, and heat-treating this gel object.

A silver coordinated complex is generated by mixing the silver ion and alkoxy group content compound which are produced by dissolving a silver salt in a nonaqueous organic solvent in nonaqueous organic solvents, such as ethanol (JP,5-213621,A).

[0005]

[Problem(s) to be Solved by the Invention]Since according to scorification it is necessary to add fusing agents to which chemical durability is reduced, such as way acid and saltpeter, to a raw material in order to make it quench and vitrify after melting, the chemical durability of the glass obtained is low. According to ion implantation given in JP,6-211619,A, expensive ion implantation equipment is required. Since silver exists in glass not in the state of an ionic state but in the state of a colloidal particle according to the sol gel process given in JP,5-213621,A, (1) A gel object cannot be heat-treated more than the melting point of (2) silver which the obtained antimicrobial glass is coloring, but there is a difficulty that precise and stable glass is not obtained and that the releasing speed of (3) silver is not loose.

[0006]So, without using an expensive device, the purpose of this invention is excellent in chemical

durability by colorlessness, and there is in providing the antimicrobial glass which can control the gradual release speed of antimicrobial.

[0007]

[Means for Solving the Problem] To achieve the above objects, antimicrobial glass of this invention, It is $\text{SiO}_2\text{-M}_x\text{O}_y$ (however, as for M, metal atom [with few the valence than the coordination number], and X and Y show atomic ratio of M and O, respectively.) system glass, and an antibacterial metal ion is contained.

[0008] A suitable method of manufacturing antimicrobial glass of this invention, A raw material solution containing a salt and water of an organic silicon compound of hydrolysis nature, a metal M compound (however, M shows a metal atom with few the valence than the coordination number when it becomes an oxide.) of hydrolysis nature, and an antibacterial metal is mixed, and it calcinates after gelling.

[0009] Each compound will hydrolyze and an organic silicon compound of hydrolysis nature and a metal M compound of hydrolysis nature will be uniformly gelled, if it mixes with water by presentation which can be vitrified by oxide conversion, respectively. If this gel is dried and calcinated, it will become $\text{SiO}_2\text{-M}_x\text{O}_y$ system glass. However, desiccation may be omitted. A grinding process may be added in one of stages before and after a baking process. If a salt of an antibacterial metal is included in a raw material solution before hydrolysis, it hydrolyzes simultaneously and antibacterial metal ion distributes uniformly in gel, and after calcination, an antibacterial metal serves as a metal ion which is tinged with positive charge (+), and exists. And since a coordination number Z twist also has few valences n of M, it exists in the circumference of M, and an oxygen atom of a surplus which is tinged with a negative charge (-) without being electrically neutralized by an electric charge (n+) of M neutralizes with antibacterial metal ion, and is stable. Therefore, an antibacterial metal exists stably and uniformly by an ionic state.

[0010] Since an antibacterial metal is distributing in glass by an ionic state, glass does not color and precise glass is obtained by high temperature firing. And since an antibacterial metal inside glass is spread toward a glass surface in an ionic state even if antibacterial metal ion is emitted and consumed from a glass surface, a releasing speed from a glass surface is continuous and loose, and proportional to root t (t: time). Inclination of a releasing speed-time graph is also controllable by ratio of the metal M and an antibacterial metal, and a total amount of an antibacterial metal.

[0011]

[Embodiment of the Invention] As for the organic silicon compound of hydrolysis nature, and the metal M compound of hydrolysis nature, what is gelled uniformly is good by adding water. The organic silicon compound of typical hydrolysis nature is an alkoxide of silicon. The metal M compound of hydrolysis nature is an organic metal M compound of hydrolysis nature like the salt of the metal M, or the alkoxide of the metal M. M is one or more sorts chosen, for example from among aluminum, La, Y, Ti, Zr, Nb, and Ta. These metal is cheap, and since it is excellent in endurance in itself, it is preferred. When it is atomic ratio $M/(\text{antibacterial metal}) \geq 1$, it is easy to ionize antibacterial metal in glass. A suitable combination sets M to aluminum and sets antibacterial metal to Ag.

[0012]

[Example]

[Manufacture of antimicrobial glass] The example of the manufacturing method of the antimicrobial glass of this invention is described with a drawing. Drawing 1 is a figure explaining the manufacturing process of antimicrobial glass.

[0013] Ethanol $\text{C}_2\text{H}_5\text{OH}$ is added to tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$ as a solvent. Separately, water, nitric acid HNO_3 , ethanol, silver nitrate AgNO_3 , aluminium nitrate 9 hydrate $\text{aluminum}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are mixed, and it is considered as a solution. It hydrolyzed having added this solution to said

tetraethoxysilane solution, and stirring it for 30 minutes, and the sol solution was prepared (drawing 1 a). The presentation of a sol solution is as being shown in Table 1.

[0014]

[Table 1]

[Mole ratio]

----- $\text{Si}(\text{OC}_2\text{H}_5)_4$ H_2O HNO_3 $\text{C}_2\text{H}_5\text{OH}$ AgNO_3 aluminum(NO_3)₃ and 9H
 O 1 8 0.01 2 0.023 0-0.115 ----- Put the sol solution into the
 container made from a plastic, and neglect it to 40 degreeC, it was made to gel after hydrolysis, and it dried for one week by 40 degreeC succeedingly after gelling (drawing 1 b). By taking out a sample from a container after desiccation, the product planet type ball mill made from zirconia grinding, and mean particle diameter being about 10 microns (drawing 1 c), putting the sample used as powder into a crucible, and calcinating by 600-1000 degreeC for 2 hours, Four kinds of glass with which aluminum/Ag mole ratios differ was generated (drawing 1 d). The presentation on the theory of the obtained glass is shown in Table 2.

[0015]

[Table 2]

ガラス No.	Al/Ag	組成 [モル%]		
		SiO ₂	Al ₂ O ₃	Ag ₂ O
A10	0	97.8	0	2.2
A11	1	95.6	2.2	2.2
A12	2	93.5	4.3	2.1
A15	5	87.9	10.1	2.0

[0016][Analysis of glass]

(1) In order to check [of the silver in glass] whether silver remains in glass next in fixed quantity, The glass obtained with the glass obtained with dry gel and the calcination temperature of 800 ** and the calcination temperature of 1000 ** was melted with about 5% of hydrofluoric acid, respectively, and the concentration of the silver in the solution was measured by high-frequency-induction joint plasma emission spectrometry. As for the concentration of the silver in the liquid melted with hydrofluoric acid, the result checked remaining without silver carrying out evaporation escaping into all the glass regardless of the addition and calcination temperature of aluminum almost in accordance with the concentration of the silver added at the time of sol preparation, as shown in drawing 2. Since the sample and the crucible welded the sample which did not add aluminum when heat-treated above 960 degreeC which is the silver melting point, heat-treatment temperature made only the sample a maximum of 950 degrees.

[0017](2) The state of the silver in glass, next the state of the silver in the glass produced by calcinating at 800 ** were analyzed by the visible ultraviolet absorption spectroscopic-analysis method. As a result, in the glass (aluminum0) which did not add aluminum, absorption was accepted near about 410 nm and this belonged with absorption by silver colloid. Since silver existed by colloid, the glass assumed yellow. On the other hand, in glass aluminum1 which added aluminum, aluminum2, and aluminum5, all three kinds of absorption were not accepted at all, but it was colorless.

[0018]The state of the silver in the glass produced by calcinating at dry gel and various temperature was analyzed in the powder X diffraction. With the glass which has not added aluminum, the peak from which calcination temperature belongs to silver above 800 degreeC was accepted. It seems that this is based on silver colloid. On the other hand, with three sorts of glass which added

aluminum, the peak at which calcination temperature belongs to silver in more than 800 degreeC was not accepted.

[0019] From the above analysis result, when the relation between a silver state and glazing structure is considered, it is as follows. Since it has the character very just like a silver ion and sodium ion, if a silver ion is added in silica glass, a silver ion will cut the network structure of silica and will be considered that one non-bridging oxygen per silver ion generates. However, since the silver ion combined with non-bridging oxygen is very unstable and it is returned easily, in the glass which does not add aluminum, the returned silver condenses and silver exists by colloid (drawing 3 upper row). On the other hand, if a trivalent element like aluminum is introduced into glass, some network silicon is replaced by aluminum, aluminum will form a tetrahedron with one negative charge superfluously, and it will be thought that a silver ion compensates this negative charge. Therefore, in the glass which added aluminum, silver configures in this tetrahedron and silver exists according to an ionic state (drawing 3 lower berth).

[0020] [The operation effect of an example]

(1) In order to evaluate the chemical durability of glass, the chemical durability of sustained-release silver valuation method profitable **** glass, and sustained-release [silver], the elution volume of silicon underwater [out of glass], aluminum, and silver was investigated in the following ways. Do not add aluminum but the glass produced by calcinating by 950 degreeC and the glass produced by adding aluminum and calcinating by 1000 degreeC are prepared, Each glass was put into 0.1g balance picking and the container of the product [exception / individual] made from polypropylene respectively, 20 ml of distilled water was added, the container was put into the incubator of 37 degreeC, and it vibrated by the turning radius of 3 cm, and the rotation frequency of 120 rpm. Glass was taken out from the prescribed period immersion back, the container was underwater picked out from the incubator, it filtered, glass and a solution were classified, giving vibration, and the concentration of silicon in the solution, aluminum, and silver was measured by high-frequency-induction joint plasma emission spectrometry. The measurement result of silicon concentration, aluminum concentration, and silver concentration is shown in drawing 4, drawing 5, and drawing 6, respectively.

[0021] (2) The elution volume of silicon increased as were shown in evaluation drawing 4 of the chemical durability of glass and the immersion period became long in the glass (aluminum0) which does not add aluminum, and the elution volume in two weeks was about 6 ppm after immersion. On the other hand, in the glass (aluminum1, aluminum2, aluminum5) which added aluminum, regardless of the quantity of the added aluminum, the elution volume of silicon increased as the immersion period became long, but. The upward tendency was quite smaller than the case where aluminum is not added, and the elution volume in two weeks was about 1.5 ppm after immersion, and when aluminum did not add, it decreased to 4 by about 1/.

[0022] As is shown [the elution volume of aluminum] in drawing 5, even if an immersion period becomes for a long time regardless of the addition of aluminum, an elution volume is almost constant, and the elution volume of aluminum in two weeks is ultralow volume after immersion. Almost not having elution of aluminum is admitted.

From these results, it is admitted by adding aluminum that the chemical durability of the glass matrix improved.

[0023] (3) As shown in sustained-release silver evaluation drawing 6, it is stair-like, the elution volume of the silver from the glass (aluminum0) which does not add aluminum increases irregularly as an immersion period becomes long, and the elution volume in two weeks is about 5 ppm after immersion.

This is equivalent to about 2.5% of silver having been eluted out of glass.

On the other hand, although silver was quickly eluted in early stages regardless of the quantity of the added aluminum in the glass (aluminum1, aluminum2, aluminum5) which added aluminum, It is eluted with the degree of about 1 constant speed after that, the elution volume of the silver in two

weeks is about 1 ppm after immersion, and this is equivalent to about 0.5% of silver having been eluted out of glass.

[0024]Next, the silver elution volume was taken along the vertical axis, square root rootd (d: immersion days) of immersion days was taken along the horizontal axis, the RBI of those values was carried out on the graph (drawing 7), and the diffuser style of the silver of three kinds of glass (aluminum1, aluminum2, aluminum5) which added aluminum was examined. As a result, in all the samples, the silver elution volume was proportional to the square root of immersion days mostly. Generally the elution volume of alkaline ion underwater from glass is proportional to the square root of time, Since it is known that this is an ion exchange reaction of the alkaline ion in glass and an underwater proton, elution of silver underwater from the glass of this example is presumed to have happened by the ion exchange reaction of the silver ion in glass, and an underwater proton.

[0025]Then, it is as follows when the diffuser style of silicon and silver is generally considered using drawing 8. First, with the glass which does not add aluminum, although silver exists as metallic colloid, since the elution volume of silicon is large, it is thought that the matrix near the surface is solved considerably. As a result, silver colloid and water contact, silver oxidizes with water, silver is eluted to underwater, the interface reaction of silver colloid and water serves as a rate determining step, and silver is considered to have been eluted irregularly (drawing 8 upper row). On the other hand with the glass which added aluminum, silver exists according to an ionic state, and there is almost no elution of silicon and aluminum. Since silver elution takes place by the ion exchange reaction of the silver ion in glass, and an underwater proton as shown previously, diffusion of a silver ion serves as a rate determining step, and is considered that silver was eluted with constant speed (drawing 8 lower berth).

[0026](4) SUTOREPUTOKOKOSU Mu wardrobe (Streptococcus mutans)ATCC25175 of the standard strain which causes a cavity easily in order to evaluate the antibacterial properties of the glass of an antibacterial evaluation example. (it is hereafter written as "S. mutans".) -- the proliferation degree was measured under coexistence of antimicrobial glass as follows.

[0027]The 5-ml TORIPUCHIKESUSO eve loss (Trypticase Soy Broth) (made by U.S. BBL.) which contains a yeast extract 0.5% It outlines the following "TSBY". Prepare and S.mutans is inoculated into it, Anaerobic culture was performed at 37 ** for 10 to 12 hours, and it prepared to 1×10^6 cells/ml in RITE ** YUSUDO transport fluid reduced transport fluid (it is hereafter written as "RTF"). aluminum/Ag separately produced by calcinating at 1000 ** carries out weighing of three kinds of antimicrobial glass, 1, 2, or 5, 0.1g, or the 0.01 g.

[0028]each antimicrobial glass -- the inside of the respectively individual above-mentioned preparation fungus liquid -- the bottom of a 37 ** anaerobic condition (10% of hydrogen, 80% of nitrogen, 10% of carbon dioxide) -- 2 and 6 -- and it was immersed for 12 hours. The preparation fungus liquid which has not immersed glass was considered as control. Serial dilution of each fungus liquid was carried out 10 times by RTF after immersion, 0.1 ml of a diluent was dropped on TSBY plate agar, anaerobic culture was performed for four days at 37 **, the plate agar to which growth of about 100 colonies was accepted was chosen from the plate agar diluted with each magnification, and number of microorganism was measured. A measurement result is shown in drawing 9.

[0029]Antibacterial properties were checked by the glass except the glass of aluminum/Ag=5/1 when a glass content was 0.1g, as shown in drawing 9. It is thought that it is because there was little silver absolute magnitude as for the difference with control having been accepted and having swarmed when the case of aluminum/Ag=5/1 and a glass content were 0.01g.

[0030]

[Effect of the Invention]The antimicrobial glass of this invention demonstrates antibacterial properties as above, and also it is colorless and excels in chemical durability and sustained-release [of the antibacterial substance]. Therefore, it can be used stably in the part which needs antibacterial properties over a long period of time.

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TECHNICAL FIELD

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PRIOR ART

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[0003]Ion implantation accommodates beforehand the glass which is the target of an ion implantation in the chamber of ion implantation equipment, and is a method of pouring the ion of antibacterial substances, such as silver, into the glass.

An ion implantation is carried out by heating and steam-izing an antibacterial substance, supplying a silver steam to inter-electrode [in a vacuum], and ionizing it (JP,6-211619,A).

[0004]A sol gel process is the method of hydrolyzing the reactant of metal alkoxide compounds, such as tetraethyl silicate, and the silver coordinated complex which configures alkoxy group content compounds, such as trimethoxysilylpropyl diethylenetriamine, adjusting a gel object, and heat-treating this gel object.

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EFFECT OF THE INVENTION

[The operation effect of an example]

(1) In order to evaluate the chemical durability of glass, the chemical durability of sustained-release silver valuation method profitable **** glass, and sustained-release [silver], the elution volume of silicon underwater [out of glass], aluminum, and silver was investigated in the following ways. Do not add aluminum but the glass produced by calcinating by 950 degreeC and the glass produced by adding aluminum and calcinating by 1000 degreeC are prepared, Each glass was put into 0.1g balance picking and the container of the product [exception / individual] made from polypropylene respectively, 20 ml of distilled water was added, the container was put into the incubator of 37 degreeC, and it vibrated by the turning radius of 3 cm, and the rotation frequency of 120 rpm. Glass was taken out from the prescribed period immersion back, the container was underwater picked out from the incubator, it filtered, glass and a solution were classified, giving vibration, and the concentration of silicon in the solution, aluminum, and silver was measured by high-frequency-induction joint plasma emission spectrometry. The measurement result of silicon concentration, aluminum concentration, and silver concentration is shown in drawing 4, drawing 5, and drawing 6, respectively.

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[Means for Solving the Problem]To achieve the above objects, antimicrobial glass of this invention, It is $\text{SiO}_2\text{-M}_x\text{O}_y$ (however, as for M, metal atom [with few the valence than the coordination number], and X and Y show atomic ratio of M and O, respectively.) system glass, and an antibacterial metal ion is contained.

[0008]A suitable method of manufacturing antimicrobial glass of this invention, A raw material solution containing a salt and water of an organic silicon compound of hydrolysis nature, a metal M compound (however, M shows a metal atom with few the valence than the coordination number when it becomes an oxide.) of hydrolysis nature, and an antibacterial metal is mixed, and it calcinates after gelling.

[0009]Each compound will hydrolyze and an organic silicon compound of hydrolysis nature and a metal M compound of hydrolysis nature will be uniformly gelled, if it mixes with water by presentation which can be vitrified by oxide conversion, respectively. If this gel is dried and calcinated, it will become $\text{SiO}_2\text{-M}_x\text{O}_y$ system glass. However, desiccation may be omitted. A grinding process may be added in one of stages before and after a baking process. If a salt of an antibacterial metal is included in a raw material solution before hydrolysis, it hydrolyzes simultaneously and antibacterial metal ion distributes uniformly in gel, and after calcination, an antibacterial metal serves as a metal ion which is tinged with positive charge (+), and exists. And since a coordination number Z twist also has few valences n of M, it exists in the circumference of M, and an oxygen atom of a surplus which is tinged with a negative charge (-) without being electrically neutralized by an electric charge (n+) of M neutralizes with antibacterial metal ion, and is stable. Therefore, an antibacterial metal exists stably and uniformly by an ionic state.

[0010]Since an antibacterial metal is distributing in glass by an ionic state, glass does not color and precise glass is obtained by high temperature firing. And since an antibacterial metal inside glass is spread toward a glass surface in an ionic state even if antibacterial metal ion is emitted and consumed from a glass surface, a releasing speed from a glass surface is continuous and loose, and proportional to roott (t: time). Inclination of a releasing speed-time graph is also controllable by ratio of the metal M and an antibacterial metal, and a total amount of an antibacterial metal.

[0011]

[Embodiment of the Invention]As for the organic silicon compound of hydrolysis nature, and the metal M compound of hydrolysis nature, what is gelled uniformly is good by adding water. The organic silicon compound of typical hydrolysis nature is an alkoxide of silicon. The metal M compound of hydrolysis nature is an organic metal M compound of hydrolysis nature like the salt of the metal M, or the alkoxide of the metal M. M is one or more sorts chosen, for example from among aluminum, La, Y, Ti, Zr, Nb, and Ta. These metal is cheap, and since it is excellent in endurance in itself, it is preferred. When it is atomic ratio $M/(\text{antibacterial metal}) \geq 1$, it is easy to ionize antibacterial metal in glass. A suitable combination sets M to aluminum and sets antibacterial metal to Ag.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]Since according to scorification it is necessary to add fusing agents to which chemical durability is reduced, such as way acid and saltpeter, to a raw material in order to make it quench and vitrify after melting, the chemical durability of the glass obtained is low. According to ion implantation given in JP,6-211619,A, expensive ion implantation equipment is required. Since silver exists in glass not in the state of an ionic state but in the state of a colloidal particle according to the sol gel process given in JP,5-213621,A, (1) A gel object cannot be heat-treated more than the melting point of (2) silver which the obtained antimicrobial glass is coloring, but there is a difficulty that precise and stable glass is not obtained and that the releasing speed of (3) silver is not loose.

[0006]So, without using an expensive device, the purpose of this invention is excellent in chemical durability by colorlessness, and there is in providing the antimicrobial glass which can control the gradual release speed of antimicrobial.

[Translation done.]

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EXAMPLE

[Example]

[Manufacture of antimicrobial glass] The example of the manufacturing method of the antimicrobial glass of this invention is described with a drawing. Drawing 1 is a figure explaining the manufacturing process of antimicrobial glass.

[0013]Ethanol C_2H_5OH is added to tetraethoxysilane $Si(OC_2H_5)_4$ as a solvent. Separately, water, nitric acid HNO_3 , ethanol, silver nitrate $AgNO_3$, aluminium nitrate 9 hydrate $aluminum(NO_3)_3 \cdot 9H_2O$ are mixed, and it is considered as a solution. It hydrolyzed having added this solution to said tetraethoxysilane solution, and stirring it for 30 minutes, and the sol solution was prepared (drawing 1 a). The presentation of a sol solution is as being shown in Table 1.

[0014]

[Table 1]

[Mole ratio]

----- $Si(OC_2H_5)_4$ H_2O HNO_3 C_2H_5OH $AgNO_3$ $aluminum(NO_3)_3$ and $9H_2O$ 1 8 0.01 2 0.023 0-0.115 -----

Put the sol solution into the container made from a plastic, and neglect it to 40 degreeC, it was made to gel after hydrolysis, and it dried for one week by 40 degreeC succeedingly after gelling (drawing 1 b). By taking out a sample from a container after desiccation, the product planet type ball mill made from zirconia grinding, and mean particle diameter being about 10 microns (drawing 1 c), putting the sample used as powder into a crucible, and calcinating by 600-1000 degreeC for 2 hours, Four kinds of glass with which aluminum/Ag mole ratios differ was generated (drawing 1 d). The presentation on the theory of the obtained glass is shown in Table 2.

[0015]

[Table 2]

ガラス No.	Al/Ag	組成 [モル%]		
		SiO ₂	Al ₂ O ₃	Ag ₂ O
A10	0	97.8	0	2.2
A11	1	95.6	2.2	2.2
A12	2	93.5	4.3	2.1
A15	5	87.9	10.1	2.0

[0016][Analysis of glass]

(1) In order to check [of the silver in glass] whether silver remains in glass next in fixed quantity,

The glass obtained with the glass obtained with dry gel and the calcination temperature of 800 ** and the calcination temperature of 1000 ** was melted with about 5% of hydrofluoric acid, respectively, and the concentration of the silver in the solution was measured by high-frequency-induction joint plasma emission spectrometry. As for the concentration of the silver in the liquid melted with hydrofluoric acid, the result checked remaining without silver carrying out evaporation escaping into all the glass regardless of the addition and calcination temperature of aluminum almost in accordance with the concentration of the silver added at the time of sol preparation, as shown in drawing 2. Since the sample and the crucible welded the sample which did not add aluminum when heat-treated above 960 degreeC which is the silver melting point, heat-treatment temperature made only the sample a maximum of 950 degrees.

[0017](2) The state of the silver in glass, next the state of the silver in the glass produced by calcinating at 800 ** were analyzed by the visible ultraviolet absorption spectroscopic-analysis method. As a result, in the glass (aluminum0) which did not add aluminum, absorption was accepted near about 410 nm and this belonged with absorption by silver colloid. Since silver existed by colloid, the glass assumed yellow. On the other hand, in glass aluminum1 which added aluminum, aluminum2, and aluminum5, all three kinds of absorption were not accepted at all, but it was colorless.

[0018]The state of the silver in the glass produced by calcinating at dry gel and various temperature was analyzed in the powder X diffraction. With the glass which has not added aluminum, the peak from which calcination temperature belongs to silver above 800 degreeC was accepted. It seems that this is based on silver colloid. On the other hand, with three sorts of glass which added aluminum, the peak at which calcination temperature belongs to silver in more than 800 degreeC was not accepted.

[0019]From the above analysis result, when the relation between a silver state and glazing structure is considered, it is as follows. Since it has the character very just like a silver ion and sodium ion, if a silver ion is added in silica glass, a silver ion will cut the network structure of silica and will be considered that one non-bridging oxygen per silver ion generates. However, since the silver ion combined with non-bridging oxygen is very unstable and it is returned easily, in the glass which does not add aluminum, the returned silver condenses and silver exists by colloid (drawing 3 upper row). On the other hand, if a trivalent element like aluminum is introduced into glass, some network silicon is replaced by aluminum, aluminum will form a tetrahedron with one negative charge superfluously, and it will be thought that a silver ion compensates this negative charge. Therefore, in the glass which added aluminum, silver configures in this tetrahedron and silver exists according to an ionic state (drawing 3 lower berth).

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a figure explaining the manufacturing process of antimicrobial glass.

[Drawing 2]It is a graph which shows the fixed-quantity value of the silver contained in antimicrobial glass.

[Drawing 3]It is a figure explaining the glass network structure of antimicrobial glass.

[Drawing 4]It is a graph which shows the underwater elution volume of silicon in the antimicrobial glass produced by calcinating at 1000 **.

[Drawing 5]It is a graph which shows the underwater elution volume of aluminum in the antimicrobial glass produced by calcinating at 1000 **.

[Drawing 6]It is a graph which shows the underwater elution volume of the silver in the antimicrobial glass produced by calcinating at 1000 **.

[Drawing 7]It is the graph which carried out the RBI of the relation between the elution volume of the above-mentioned silver, and the square root of immersion days.

[Drawing 8]It is a figure explaining a diffuser style underwater [silver].

[Drawing 9]It is a graph which shows the degree of antibacterial properties of antimicrobial glass.

[Translation done.]

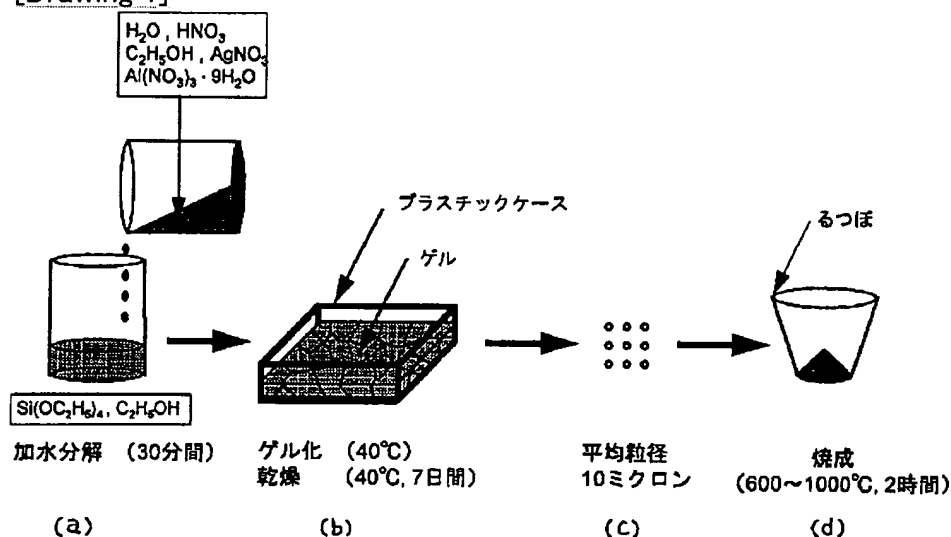
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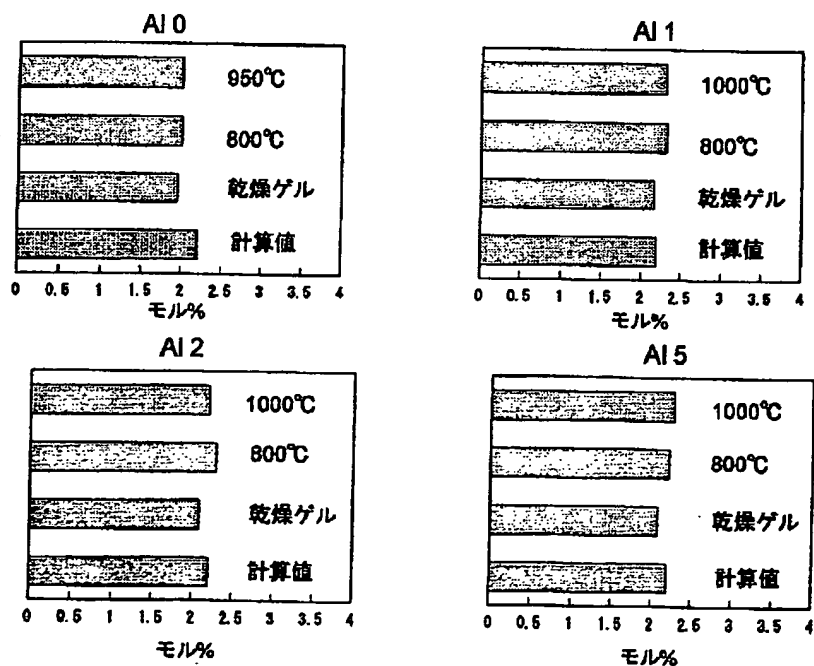
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DRAWINGS

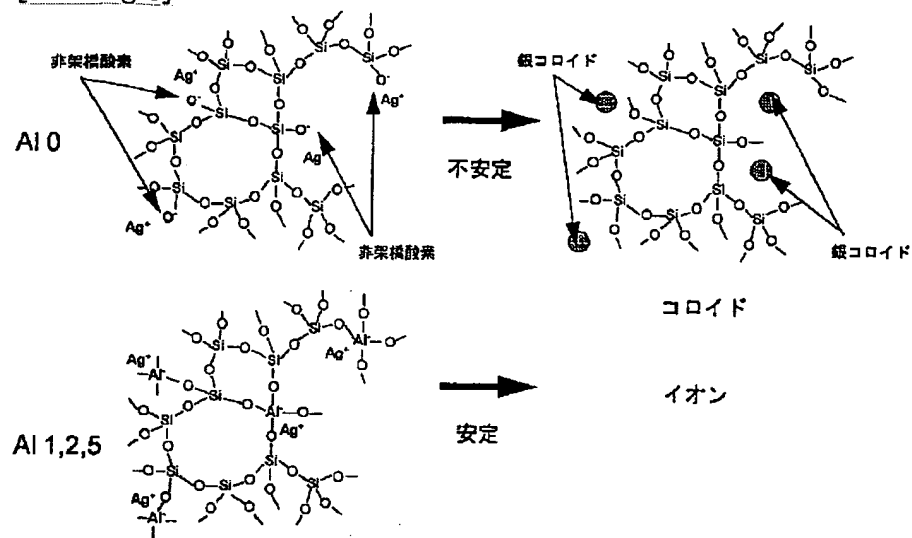
[Drawing 1]



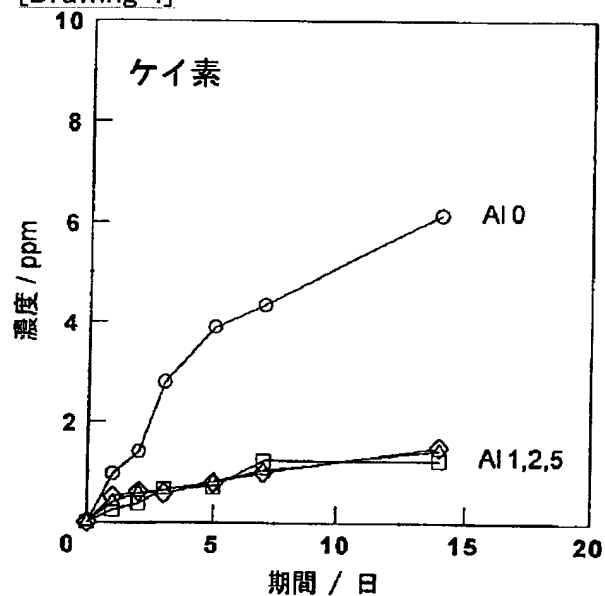
[Drawing 2]



[Drawing 3]

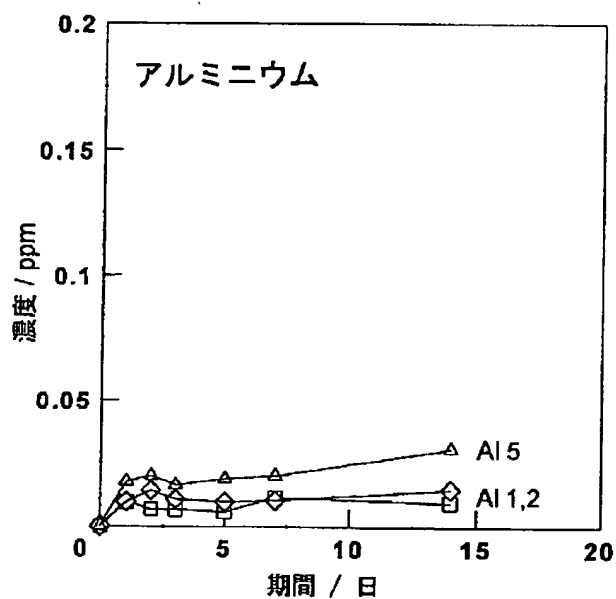


[Drawing 4]



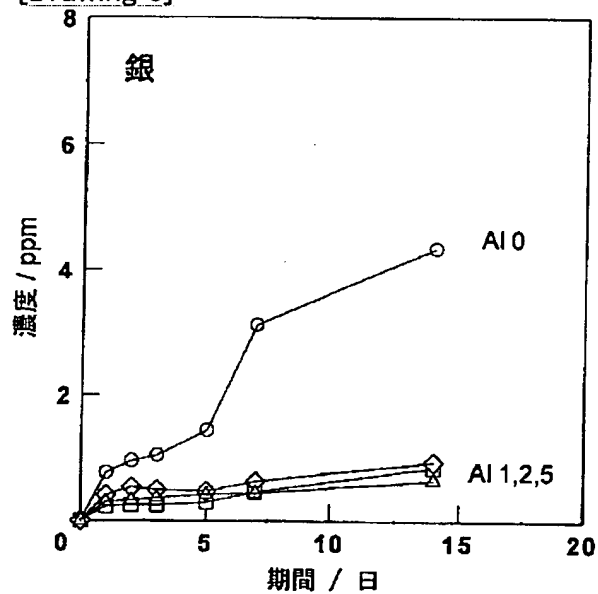
1000°Cで焼成して得られた抗菌性ガラス
中のケイ素の水中への溶出量

[Drawing 5]



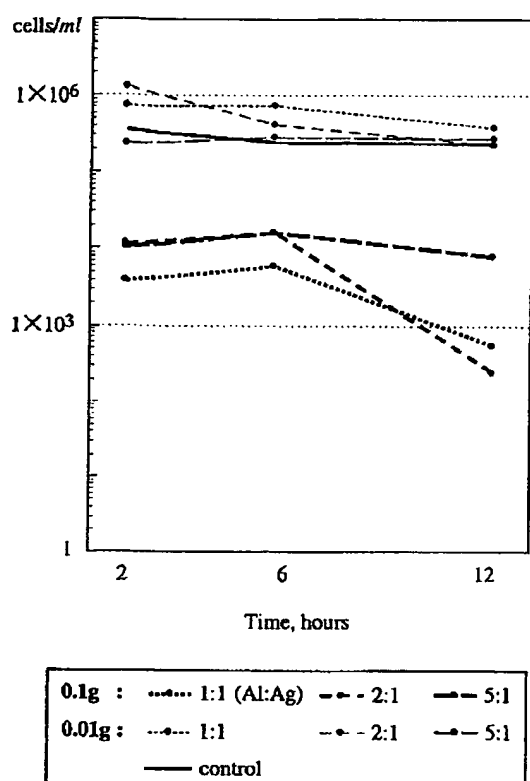
1000°Cで焼成して得られた抗菌性ガラス
中のアルミニウムの水中への溶出量

[Drawing 6]

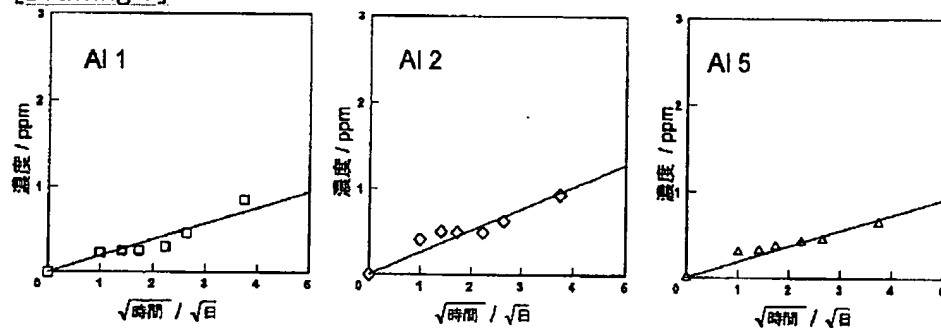


1000°Cで焼成して得られた抗菌性ガラス
中の銀の水中への溶出量

[Drawing 9]

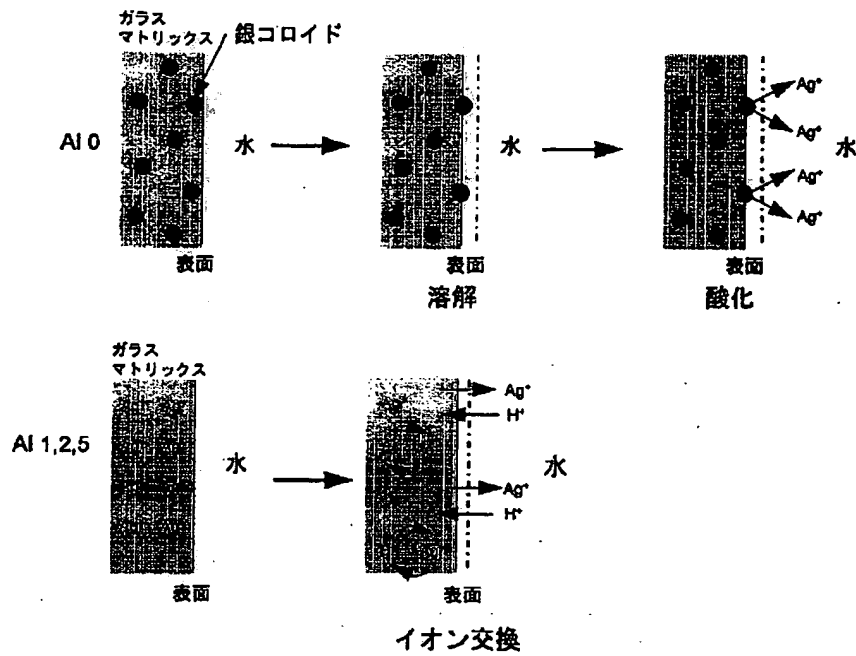


[Drawing 7]



1000°Cで焼成して得られた抗菌性ガラス中の銀の
水中への溶出量と浸漬日数の平方根との関係

[Drawing 8]



[Translation done.]

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(71) 出願人 591268508

財団法人イオン工学振興財団

京都府京都市左京区吉田河原町14 近畿地方発明センター内

(72) 発明者 小久保 正

京都府長岡京市梅が丘2丁目50番地

(72) 発明者 山本 宏治

岐阜県岐阜市鷺山2563番地

(72) 発明者 宮路 史明

京都府京都市伏見区桃山町泰長老宮有地

桃山東合町35号

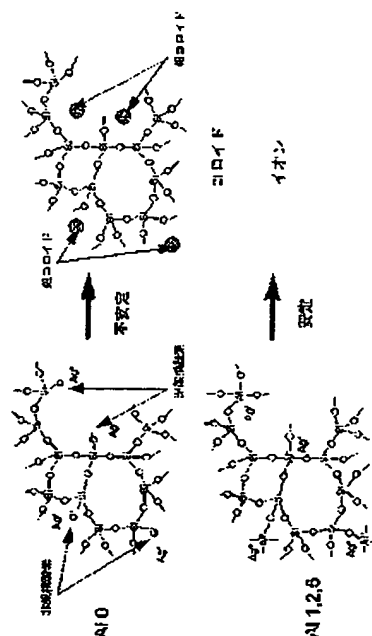
(74) 代理人 弁護士 矢野 正行

(54) 【発明の名称】 抗菌性ガラス及びその製造方法

(57) 【要約】

【課題】 高価な装置を用いることなく、無色で化学的耐久性に優れ、抗菌物質の徐放速度を制御できる抗菌性ガラスを提供する。

【解決手段】 テトラエトキシシラン等の加水分解性の有機ケイ素化合物、硝酸アルミニウム等の加水分解性の金属M化合物（ただし、Mは酸化物となったときにその価数が配位数よりも少ない金属原子を示す。）、硝酸銀等の抗菌性金属の塩及び水を含む原料溶液を混合し、ゲル化後、焼成することを特徴とする。



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【特許請求の範囲】

【請求項1】 $S_iO_2-M_nO_r$ （ただし、Mはその価数が配位数よりも少ない金属原子、XとYはそれぞれMとOの原子比を示す。）系ガラスであって、抗菌性の金属イオンを含有することを特徴とする抗菌性ガラス。

【請求項2】 Mが、Al、La、Y、Ti、Zr、Nb及びTaのうちから選ばれる1種以上である請求項1に記載の抗菌性ガラス。

【請求項3】 原子比M/（抗菌性の金属） ≥ 1 である請求項1又は2に記載の抗菌性ガラス。

【請求項4】 MがAl、抗菌性の金属がAgである請求項1～3のいずれかに記載の抗菌性ガラス。

【請求項5】 加水分解性の有機ケイ素化合物、加水分解性の金属M化合物（ただし、Mは酸化物となったときにその価数が配位数よりも少ない金属原子を示す。）、抗菌性金属の塩及び水を含む原料溶液を混合し、ゲル化後、焼成することを特徴とする抗菌性ガラスの製造方法。

【請求項6】 Mが、Al、La、Y、Ti、Zr、Nb及びTaのうちから選ばれる1種以上である請求項5に記載の抗菌性ガラスの製造方法。

【請求項7】 原子比M/（抗菌性の金属） ≥ 1 である請求項5又は6に記載の抗菌性ガラスの製造方法。

【請求項8】 MがAl、抗菌性の金属がAgである請求項5～7のいずれかに記載の抗菌性ガラスの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、抗菌性ガラス及びその製造方法に属する。この発明の抗菌性ガラスは、歯科修復用コンポジットレジン（コンポジット）のフィラー、生体骨修復用セメントのフィラー、カテーテルのフィラー、塗料、水の殺菌剤等に好適に利用される。

【0002】

【従来の技術】従来、抗菌性ガラスの製造方法としては、熔融法、イオン注入法及びゾルゲル法が本件出願前の最新技術として知られている。熔融法は、一般的なガラス製造法であって、例えばガラス原料となるケイ酸、ほう酸等の酸化物粉末を酸化銀と混合し、熔融した後、急冷してガラス化する。

【0003】イオン注入法は、予めイオン注入装置のチャンパーにイオン注入の対象となるガラスを収容しておき、銀等の抗菌性物質のイオンをそのガラスに注入する方法であり、抗菌性物質を加熱して蒸気化し、銀蒸気を真空中の電極間に供給してイオン化することによって、イオン注入する（特開平6-211619号）。

【0004】ゾルゲル法は、テトラエチルシリケート等の金属アルコキシド化合物と、トリメトキシシリルプロピルジエチレントリアミン等のアルコキシ基含有化合物を配位してなる銀配位化合物との反応物を加水分解して

ゲル体を調整し、該ゲル体を熱処理する方法であり、銀配位化合物は、銀塩を非水有機溶媒に溶解して得られる銀イオンとアルコキシ基含有化合物とをエタノール等の非水有機溶媒中で混合することによって生成する（特開平5-213621号）。

【0005】

【発明が解決しようとする課題】熔融法によれば、熔融後に急冷してガラス化させるために、化学的耐久性を低下させるほう酸や硼酸等の融剤を原料に加える必要があるので、得られるガラスの化学的耐久性が低い。特開平6-211619号に記載のイオン注入法によれば、高価なイオン注入装置が必要である。特開平5-213621号に記載のゾルゲル法によれば、銀がイオン状態ではなく、コロイド粒子状態でガラス中に存在するので、(1)得られた抗菌性ガラスが着色している、(2)銀の融点以上にゲル体を熱処理できず、緻密で安定なガラスが得られない、(3)銀の放出速度が緩やかでない、といった難点がある。

【0006】それ故、この発明の目的は、高価な装置を用いることなく、無色で化学的耐久性に優れ、抗菌物質の徐放速度を制御できる抗菌性ガラスを提供することにある。

【0007】

【課題を解決するための手段】上記目的を達成するために、この発明の抗菌性ガラスは、 $S_iO_2-M_nO_r$ （ただし、Mはその価数が配位数よりも少ない金属原子、XとYはそれぞれMとOの原子比を示す。）系ガラスであって、抗菌性の金属イオンを含有することを特徴とする。

【0008】この発明の抗菌性ガラスを製造する適切な方法は、加水分解性の有機ケイ素化合物、加水分解性の金属M化合物（ただし、Mは酸化物となったときにその価数が配位数よりも少ない金属原子を示す。）、抗菌性金属の塩及び水を含む原料溶液を混合し、ゲル化後、焼成することを特徴とする。

【0009】加水分解性の有機ケイ素化合物と加水分解性の金属M化合物とを、それぞれ酸化物換算でガラス化可能な組成で水とともに混合すると、各化合物が加水分解して均一にゲル化する。このゲルを乾燥し焼成すると、 $S_iO_2-M_nO_r$ 系ガラスとなる。ただし、乾燥は省略しても良い。焼成工程の前段いずれかの段階で粉砕工程を追加しても良い。加水分解前の原料溶液に抗菌性金属の塩を含ませると、同時に加水分解して抗菌性金属イオンがゲル中に均一に分散し、焼成後に抗菌性金属が正電荷（+）を帯びた金属イオンとなって存在する。そして、Mの価数nが配位数2よりも少ないので、Mの電荷（n+）で電気的に中和されずに負電荷（-）を帯びた余剰の酸素原子がMの周囲に存在し、抗菌性金属イオンと中和して安定化する。従って、抗菌性金属がイオン状態で安定且つ均一に存在する。

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【0010】抗菌性金属がイオン状態でガラス中に分散しているため、ガラスが着色しないし、高温焼成により緻密なガラスが得られる。そして、ガラス表面から抗菌性金属イオンが放出され消費されても、ガラス内部の抗菌性金属がイオン状態でガラス表面に向かって拡散するので、ガラス表面からの放出速度は連続的且つ緩やかで、 \sqrt{t} (t :時間) に比例する。金属Mと抗菌性金属との比及び抗菌性金属の総量で放出速度-時間グラフの勾配を制御することもできる。

【0011】

【発明の実施の形態】加水分解性の有機ケイ素化合物と加水分解性の金属M化合物は、水を加えることによって、均一にゲル化するものが良い。典型的な加水分解性の有機ケイ素化合物は、ケイ素のアルコキシドである。また、加水分解性の金属M化合物は、金属Mの塩もしくは金属Mのアルコキシドのような加水分解性の有機金属M化合物である。Mは、例えばAl、La、Y、Ti、Zr、Nb及びTaのうちから選ばれる1種以上である。これらの金属は、安価でそれ自体耐久性に優れる*

*で好ましい。原子比M/(抗菌性の金属) ≥ 1 であるとき、抗菌性の金属がガラス中でイオン化しやすい。好適な組み合わせは、MをAl、抗菌性の金属をAgとするものである。

【0012】

【実施例】

【抗菌性ガラスの製造】この発明の抗菌性ガラスの製造方法の実施例を図面とともに説明する。図1は、抗菌性ガラスの製造過程を説明する図である。

10 【0013】テトラエトキシシラン $\text{Si}(\text{OC}_2\text{H}_5)_4$ にエタノール $\text{C}_2\text{H}_5\text{OH}$ を溶媒として加える。別途、水、硝酸 HNO_3 、エタノール、硝酸銀 AgNO_3 、硝酸アルミニウム9水和物 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ を混合して溶液とする。この溶液を前記テトラエトキシシラン溶液に加えて30分間攪拌しながら加水分解を行い、ゾル溶液を調製した(図1a)。ゾル溶液の組成は、表1に示す通りである。

【0014】

【表1】

[モル比]

$\text{Si}(\text{OC}_2\text{H}_5)_4$	H_2O	HNO_3	$\text{C}_2\text{H}_5\text{OH}$	AgNO_3	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
1	8	0.01	2	0.023	0~0.115

加水分解後、ゾル溶液をプラスチック製の容器に入れて40℃に放置してゲル化させ、ゲル化後引き続いて40℃で1週間乾燥した(図1b)。乾燥後、試料を容器から取り出し、シリコン製遊星型ボールミルで粉砕し、平均粒径を約10ミクロンとし(図1c)、粉末となった試料をろつばに入れて600~1000℃で2時間焼成すること※30

※によって、Al/Agモル比の異なる4種類のガラスを生成した(図1d)。得られたガラスの理論上の組成を表2に示す。

【0015】

【表2】

ガラス No.	Al/Ag	組成 [モル%]		
		SiO_2	Al_2O_3	Ag_2O
A10	0	97.8	0	2.2
A11	1	95.6	2.2	2.2
A12	2	93.5	4.3	2.1
A15	5	87.9	10.1	2.0

【0016】【ガラスの分析】

(1) ガラス中の銀の定量

次にガラス中に銀が残存するか否かを確認するために、乾燥ゲル、焼成温度800℃で得られたガラス及び焼成温度1000℃で得られたガラスをそれぞれ約5%のフッ化水素酸で溶かし、その溶液中の銀の濃度を高周波誘導結合プラズマ発光分析により測定した。その結果、フッ化水素酸で溶かした液中の銀の濃度は、図2に示すようにアルミニウムの添加量及び焼成温度に関係なく、ゾル調製時に添加した銀の濃度とほぼ一致し、全てのガラス中に銀が蒸発逃散することなく残存していることが確

40 認された。尚、アルミニウムを添加しなかった試料を銀の融点である960℃以上で加熱処理を行ったところ、試料とろつばが融着したため、同試料のみ加熱処理温度は最大950℃とした。

【0017】(2) ガラス中の銀の状態

次に、800℃で焼成して得られたガラス中の銀の状態を可視紫外吸収分光分析法にて分析した。その結果、アルミニウムを添加しなかったガラス(A10)では、約410nm付近に吸収が認められ、これは銀コロイドによる吸収と帰属された。尚、同ガラスは銀がコロイド状態で存在する為、黄色を呈した。一方、アルミニウムを添加したガ

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ラスA11,A12,A15では、3種類とも全く吸収が認められず、無色であった。

【0018】また、乾燥ゲル及び種々の温度で焼成して得られたガラス中の銀の状態を粉末X線回折にて分析した。アルミニウムを添加していないガラスでは焼成温度が800℃以上で銀に帰属されるピークが認められた。これは銀コロイドによるものと思われる。一方、アルミニウムを添加した3種のガラスでは焼成温度が800℃以上でも銀に帰属されるピークは認められなかった。

【0019】以上の分析結果より、銀の状態とガラス構造との関係について考察すると以下ようになる。銀イオンとナトリウムイオンと非常に似た性質を持っているので、銀イオンをシリカガラス中に添加すると、銀イオンがシリカの網目構造を切断し、銀イオン1つ当たり1つの非架橋酸素が生成すると思われる。しかし、非架橋酸素に結合している銀イオンは非常に不安定で容易に還元されるため、アルミニウムを添加しないガラスでは、還元された銀が凝集し、銀がコロイド状態で存在する(図3上段)。一方、アルミニウムのような3価の元素をガラス中に導入すると、ネットワークのケイ素が一部アルミニウムに置換され、アルミニウムは1つの負電荷を過剰に有した四面体を形成し、この負電荷を銀イオンが補償すると考えられる。従って、アルミニウムを添加したガラスでは、銀がこの四面体に配位し、銀がイオン状態で存在する(図3下段)。

【0020】[実施例の作用効果]

(1) ガラスの化学的耐久性と銀の徐放性の評価方法
得られたガラスの化学的耐久性及び銀の徐放性を評価するために、以下の要領でガラス中から水中へのケイ素、アルミニウム及び銀の溶出量を調べた。アルミニウムを添加せず950℃で焼成して得られたガラス、アルミニウムを添加して1000℃で焼成して得られたガラスを準備し、各ガラスを0.1g秤取り、それぞれ個別にポリプロピレン製の容器に入れ、蒸留水を20ml添加し、容器を37℃の恒温槽に入れ、回転半径3cm、回転頻度120rpmで振動した。振動を与えながらガラスを水中に所定期間浸漬後、容器を恒温槽より取り出し、濾過してガラスと溶液とを分別し、同溶液中のケイ素、アルミニウム及び銀の濃度を高周波誘導結合プラズマ発光分析により測定した。ケイ素濃度、アルミニウム濃度及び銀濃度の測定結果をそれぞれ図4、図5及び図6に示す。

【0021】(2) ガラスの化学的耐久性の評価

図4に示されるように、アルミニウムを添加しないガラス(A10)では、浸漬期間が長くなるにつれてケイ素の溶出量が増加し、浸漬後2週間における溶出量は約5ppmであった。一方、アルミニウムを添加したガラス(A11,A12,A15)では、添加したアルミニウムの量に関係なく、浸漬期間が長くなるにつれてケイ素の溶出量は増加したが、その増加傾向はアルミニウムを添加しない場合よりかなり小さく、浸漬後2週間における溶出量は約1.5ppmで、

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アルミニウムの添加しない場合の約1/4に減少した。

【0022】アルミニウムの溶出量は、図5に示されるようにアルミニウムの添加量に関係なく浸漬期間が長くなっても溶出量はほぼ一定で、浸漬後2週間におけるアルミニウムの溶出量は極微量であり、アルミニウムの溶出はほとんどないものと認められる。これらの結果より、アルミニウムを添加することによって、ガラスマトリックスの化学的耐久性は向上したと認められる。

【0023】(3) 銀の徐放性の評価

図6に示されるように、アルミニウムを添加しないガラス(A10)からの銀の溶出量は、浸漬期間が長くなるにつれて階段状で不規則に増加し、浸漬後2週間における溶出量は約5ppmであり、これはガラス中から約2.5%の銀が溶出したことに相当する。一方、アルミニウムを添加したガラス(A11,A12,A15)では、添加したアルミニウムの量に関係なく、銀は初期には急速に溶出したが、その後はほぼ一定速度で溶出し、浸漬後2週間における銀の溶出量は約1ppmであり、これはガラス中から約0.5%の銀が溶出したことに相当する。

【0024】次に、縦軸に銀の溶出量、横軸に浸漬日数の平方根 \sqrt{d} (d :浸漬日数)をとり、それらの値をグラフ上に打点し(図7)、アルミニウムを添加した3種類のガラス(A11,A12,A15)の銀の溶出機構について検討した。その結果、全ての試料において銀の溶出量は浸漬日数の平方根にほぼ比例した。一般に、ガラスから水中へのアルカリイオンの溶出量は時間の平方根に比例し、これはガラス中のアルカリイオンと水中のプロトンとのイオン交換反応であることが知られていることから、本実施例のガラスから水中への銀の溶出は、ガラス中の銀イオンと水中のプロトンとのイオン交換反応により起こっているものと推定される。

【0025】そこで、ケイ素及び銀の溶出機構について図8を用いて全般的に考察すると以下ようになる。まず、アルミニウムを添加しないガラスでは、銀が金属コロイドとして存在するが、ケイ素の溶出量が大いことから、表面付近のマトリックスはかなり解けていると考えられる。その結果、銀コロイドと水とが接触し、銀が水によって酸化され、銀は水中へ溶出し、銀コロイドと水との界面反応が律速段階となり、銀が不規則に溶出したものと思われる(図8上段)。一方、アルミニウムを添加したガラスでは、銀はイオン状態で存在し、ケイ素及びアルミニウムの溶出はほとんどない。銀の溶出は、先に示したように、ガラス中の銀イオンと水中のプロトンとのイオン交換反応により起こるので、銀イオンの拡散が律速段階となり、銀が一定速度で溶出したと考えられる(図8下段)。

【0026】(4) 抗菌性の評価

実施例のガラスの抗菌性を評価するために、虫歯の原因となりやすい基準菌株のストレプトコッカス(Streptococcus mutans)ATCC25175(以下、「S.mutans」と略記す

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る。)の増殖度を以下のように抗菌性ガラスの共存下で測定した。

【0027】0.5%酵母エキスを含む5 mlのトリプティック・ soja ブロス (Trypticase Soy Broth) (米国BBL社製、以下「TSBY」と略記する。)を準備し、それにS.mutansを接種し、37℃で10～12時間嫌気培養を行い、リユー・トランスポート・フルイド (reduced transport fluid) (以下、「RTF」と略記する。)にて 1×10^6 cells/mlに調製した。別途、1000℃で焼成して得られたA1/Agが1、2又は5の3種類の抗菌性ガラス0.1gもしくは0.01gを秤量する。

【0028】各々の抗菌性ガラスをそれぞれ個別の上記調製菌液中に37℃の嫌気条件下(水素10%、窒素80%、二酸化炭素10%)で2、6及び12時間浸漬した。また、ガラスを浸漬していない調製菌液をコントロールとした。浸漬後、各菌液をRTFで10倍連続希釈し、希釈液の0.1mlをTSBY平板培地上に滴下し、37℃で4日間嫌気培養を行い、各倍率で希釈した平板培地の中から100個程度のコロニーの発育が認められた平板培地を選んで菌数を測定した。測定結果を図9に示す。

【0029】図9に示されるように、ガラス量が0.1gの場合は、A1/Ag=5/1のガラスを除くガラスに抗菌性が確認された。A1/Ag=5/1の場合とガラス量が0.01gの場合にコントロールとの差が認め

*られたかったのは、銀の絶対量が少なかったためであると考えられる。

【0030】

【発明の効果】以上の通り、この発明の抗菌性ガラスは、抗菌性を発揮するうえ、無色で、化学的耐久性及び抗菌性物質の徐放性にすぐれている。従って、抗菌性を必要とする個所で長期安定的に使用することができる。

【図面の簡単な説明】

【図1】 抗菌性ガラスの製造過程を説明する図である。

【図2】 抗菌性ガラスに含まれる銀の定置値を示すグラフである。

【図3】 抗菌性ガラスのガラス網目構造を説明する図である。

【図4】 1000℃で焼成して得られた抗菌性ガラス中のケイ素の水の中への溶出量を示すグラフである。

【図5】 1000℃で焼成して得られた抗菌性ガラス中のアルミニウムの水の中への溶出量を示すグラフである。

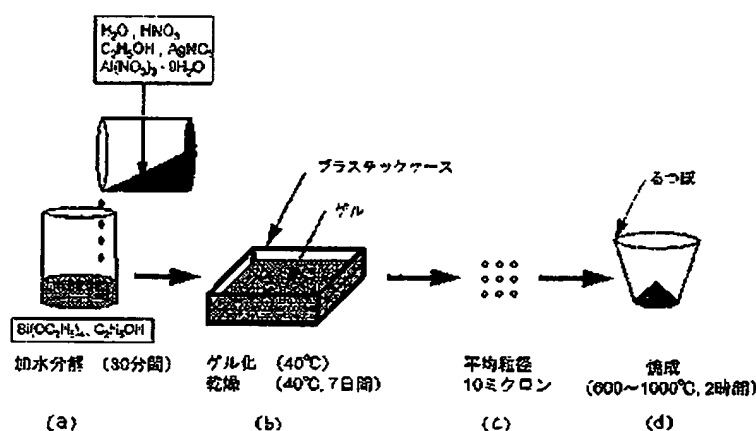
【図6】 1000℃で焼成して得られた抗菌性ガラス中の銀の水の中への溶出量を示すグラフである。

【図7】 上記銀の溶出量と浸漬日数の平方根との関係を示したグラフである。

【図8】 銀の水の中への溶出機構を説明する図である。

【図9】 抗菌性ガラスの抗菌度を示すグラフである。

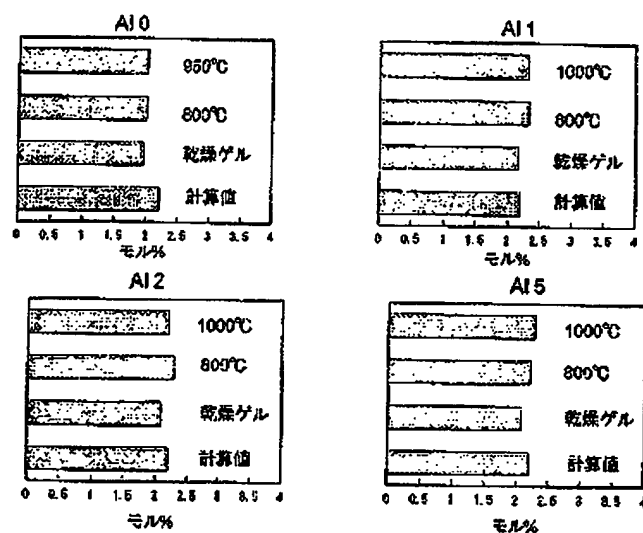
【図1】



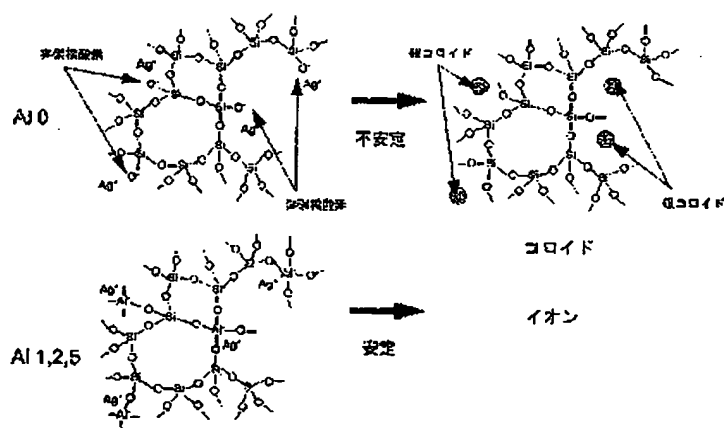
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【図2】



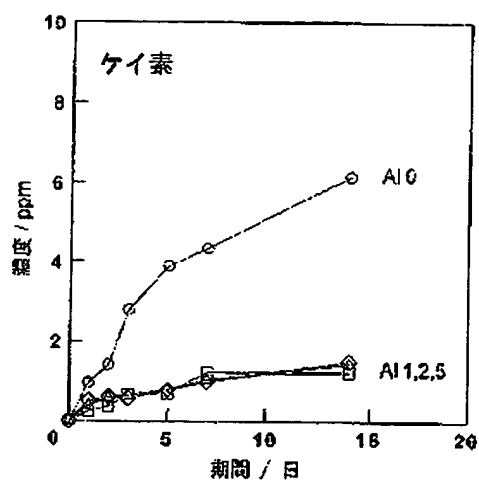
【図3】



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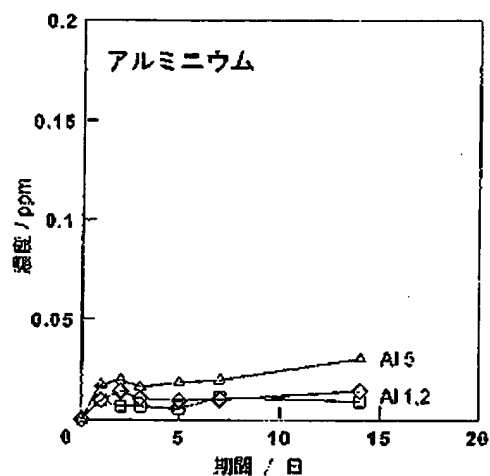
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【図4】



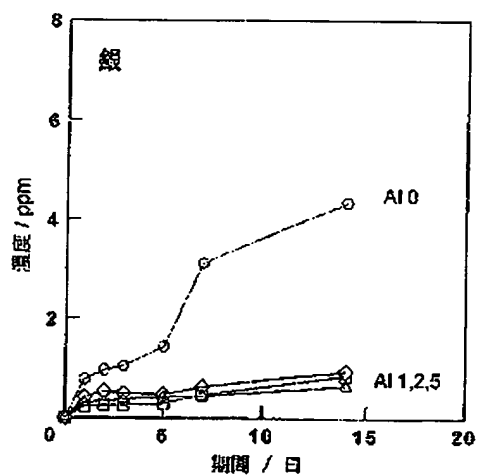
1000℃で焼成して得られた抗菌性ガラス
中のケイ素の水中への溶出量

【図5】



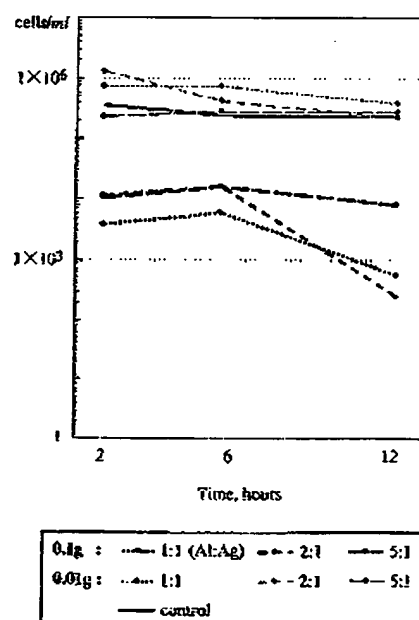
1000℃で焼成して得られた抗菌性ガラス
中のアルミニウムの水中への溶出量

【図6】



1000℃で焼成して得られた抗菌性ガラス
中の銀の水中への溶出量

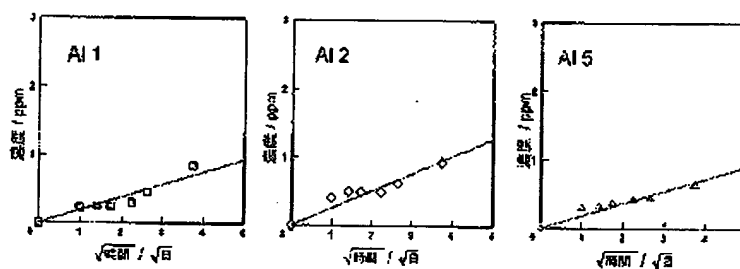
【図9】



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【図7】



1000℃で焼成して得られた抗菌性ガラス中の銀の
水中への溶出量と浸漬日数の平方根との関係

【図8】

